

CLAIMS

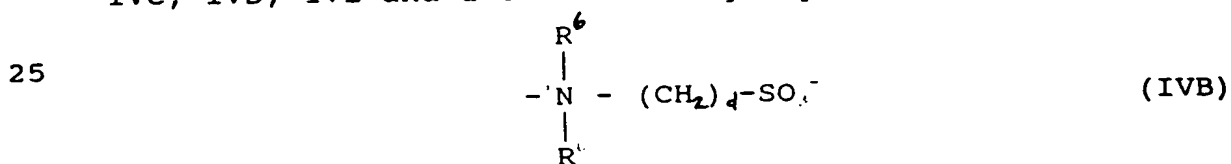
1. A process in which a substrate having a surface which bears substrate pendant functional groups is coated with a coating composition containing a polymer formed from a radical polymerisable monomers including a radical polymerisable zwitterionic monomer and a radical polymerisable monomer containing a reactive group to form a polymer having zwitterionic groups and pendant reactive groups and the said pendant reactive groups are reacted to form covalent bonds with said substrate pendant functional group and thereby form a stable coating of polymer on the said surface, and wherein

said zwitterionic monomer has the general formula I



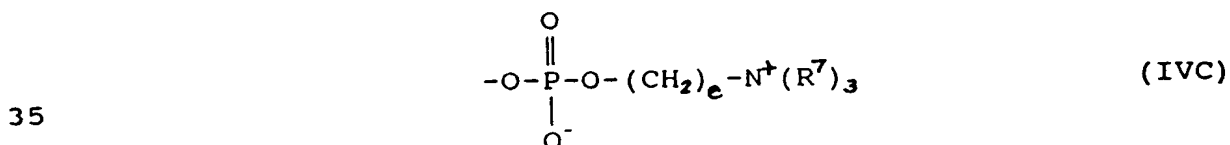
wherein B is a straight or branched alkylene, oxaalkylene or oligo-oxaalkylene chain optionally containing one or more fluorine atoms up to and including perfluorinated chains, or if X contains a carbon-carbon chain between B and the centre of permanent position charge or if Y contains a terminal carbon atom bonded to B, a valence bond;

X is a zwitterionic group selected from groups IVB, IVC, IVD, IVE and IVF in which group IVB has the formula



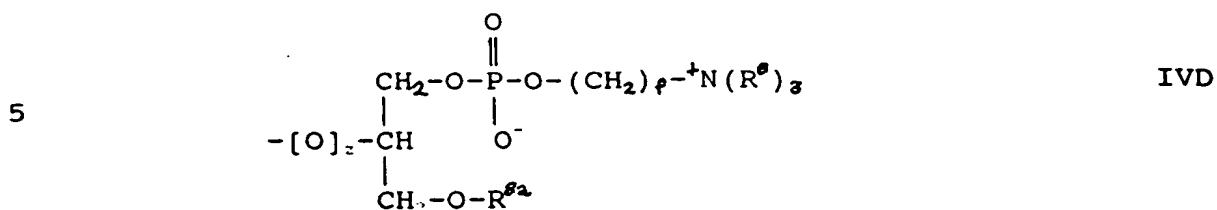
wherein the groups R^6 are the same or different and each is hydrogen or C_{1-4} alkyl and d is from 2 to 4;

group IVC has the formula



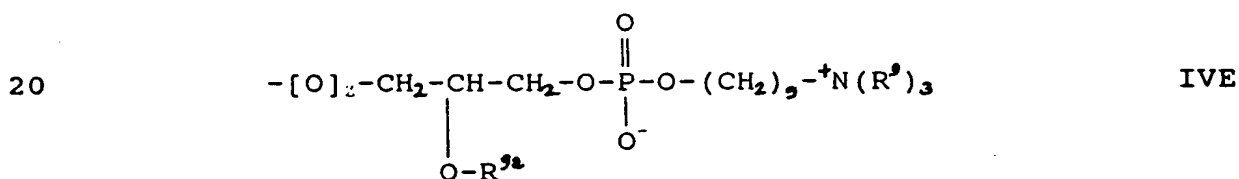
where the groups R^7 are the same or different and each is hydrogen or C_{1-4} alkyl, and e is from 1 to 4;

group IVD has the formula



wherein the groups R^g are the same or different and each is hydrogen or C_{1-4} alkyl, R^{8a} is hydrogen or a group -C(O)B^1R^{8b} wherein R^{8b} is hydrogen or methyl, B^1 is a valence bond or straight or branched alkylene, oxaalkylene or oligo-oxaalkylene group, and f is from 1 to 4; and if B is other than a valence bond z is 1 and if B is a valence bond z is 0, if X is directly bonded to an oxygen or nitrogen atom and otherwise z is 1;

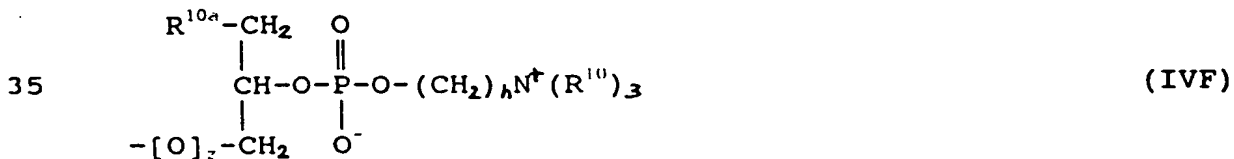
group IVE has the formula



wherein the groups R^g are the same or different and each is hydrogen or C_{1-4} alkyl, R^{9a} is hydrogen or a group -C(O)B^2R^{9b} , wherein R^{9b} is hydrogen or methyl, B^2 is a valence bond or a straight or branched alkylene, oxaalkylene or oligo-oxaalkylene group, and g is from 1 to 4; and

if B is other than a valence bond z is 1 and if B is a valence bond z is 0 if X is directly bonded to an oxygen or nitrogen atom and otherwise z is 1; and

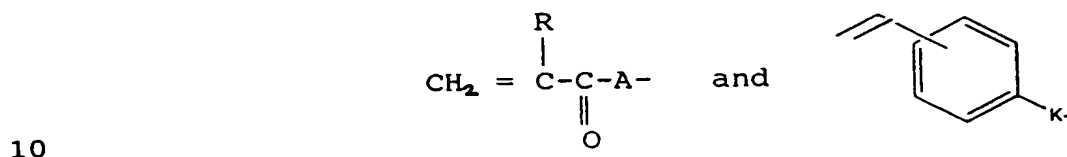
group IVF has the formula



wherein the groups R^{10} are the same or different and each is hydrogen or C_{1-4} alkyl, R^{10a} is hydrogen or a group -C(O)B^3R^{10b} wherein R^{10b} is hydrogen or methyl, B^3 is a valence bond or a straight or branched alkylene, oxaalkylene or oligo-oxaalkylene group, and h is from 1 to 4; and

if B is other than a valence bond z is 1 and if B is a valence bond z is 0 if X is directly bonded to the oxygen or nitrogen and otherwise z is 1; and

Y is an ethylenically unsaturated polymerisable group
5 selected from



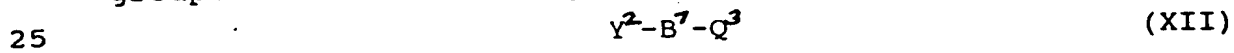
wherein:

R is hydrogen or a C₁-C₄ alkyl group;

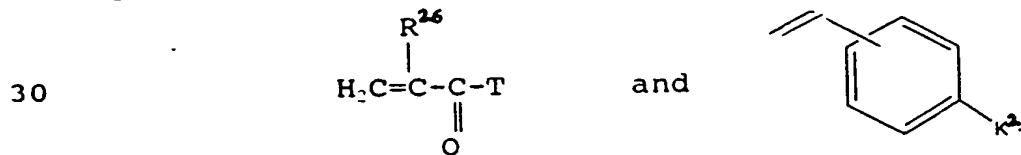
A is -O- or -NR¹- where R¹ is hydrogen or a C₁-C₄ alkyl
15 group or R¹ is -B-X where B and X are as defined above; and

K is a group -(CH₂)_pOC(O)-, -(CH₂)_pC(O)O-, -(CH₂)_pOC(O)O-, -(CH₂)_pNR²-, -(CH₂)_pNR²C(O)-, -CH₂)_pC(O)NR²-, -(CH₂)_pNR²C(O)O-, -(CH₂)_pOC(O)NR²-, -(CH₂)_pNR²C(O)NR²-, (in
20 which the groups R² are the same or different) -(CH₂)_pO-, -(CH₂)_pSO₃-, or, optionally in combination with B, a valence bond and p is from 1 to 12 and R² is hydrogen or a C₁-C₄ alkyl group, and

said radical polymerisable monomer containing reactive groups has the formula general formula (XII)



where Y² is an ethylenically unsaturated polymerisable group selected from



where R²⁶ is hydrogen or C₁-C₄ alkyl;

35 T is -O- or NR²⁷-, wherein R²⁷ is hydrogen or a C₁-C₄ alkyl group or R²⁷ is a group -B⁷Q³;

B⁷ is a valence bond a straight or branched alkylene oxaalkylene or oligo-oxaalkylene group;

40 K² is a group -(CH₂)_qOC(O)-, -(CH₂)_qC(O)O-, -(CH₂)_qOC(O)O-, -(CH₂)_qNR²⁰-, -(CH₂)_qNR²⁰C(O)-,

$-(CH_2)_qC(O)NR^{20}-$, $-(CH_2)_qNR^{20}C(O)O-$, $-(CH_2)_qOC(O)NR^{20}-$,
 $-(CH_2)_qNR^{20}C(O)NR^{20}-$ (in which the groups R^{20} are the same or
 different), $-(CH_2)_qO-$, or $-(CH_2)_qSO_3-$, or a valence bond and
 q is from 1 to 12 and R^{20} is hydrogen or a C_1-C_4 alkyl
 5 group; and

Q^3 is a reactive group selected from the group
 consisting of aldehyde groups; silane and siloxane groups
 containing one or more substituents selected from halogen
 atoms and C_{1-4} -alkoxy groups; hydroxyl; amino; carboxyl;
 10 epoxy; $-CHOHCH_2Hal$ (in which Hal is selected from chlorine,
 bromine and iodine atoms); succinimido; tosylate; triflate;
 imidazole carbonyl amino; optionally substituted triazine
 groups; acetoxy; mesylate; carbonyl di(cyclo)alkyl
 carbodiimidoyl; and oximino.

15 2. A process according to claim 1 in which Q^3 is selected
 from the group consisting of aldehyde, reactive silane and
 siloxane amino, epoxy, $CHOHCH_2Hal$ (in which Hal is
 halogen), succinimido, tosylate, triflate,
 imidazolecarbonyl amino and optionally substituted triazine
 20 groups.

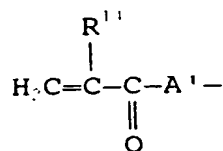
3. A process according to claim 1 in which the surface
 pendant groups are selected from the group consisting of
 hydroxyl, carboxyl and amine groups.

4. A process according to claim 1 in which the polymer is
 25 formed from 2-(methacryloyloxyethyl)-2'-(trimethylammonium)
 ethyl phosphate inner salt and 2-aminoethylmethacrylate and
 in which the covalent bonding of the pendant amino group is
 to a surface having pendant carboxylate groups is achieved
 through the formation of an amide linkage.

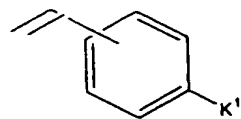
30 5. A process according to claim 1 in which the said
 radical polymerisable monomers include a comonomer of the
 general formula VI



where Y' is an ethylenically unsaturated polymerisable
 35 group selected from



and



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where R^{14} is selected from the group consisting of hydrogen and C_1 - C_4 alkyl,

A' is $-\text{O}-$ or $-\text{NR}^{15}-$ where R^{15} is selected from the group consisting of hydrogen, C_1 - C_4 alkyl groups and groups

10 Q;

K^1 is selected from the group consisting of $-(\text{CH}_2)_1\text{OC}(\text{O})-$, $-(\text{CH})_1\text{C}(\text{O})\text{O}-$, $-(\text{CH}_2)_1\text{OC}(\text{O})\text{O}-$, $-(\text{CH}_2)_1\text{NR}^{16}-$, $-(\text{CH}_2)_1\text{NR}^{16}\text{C}(\text{O})-$, $-(\text{CH}_2)_1\text{C}(\text{O})\text{NR}^{16}-$, $-(\text{CH}_2)_1\text{NR}^{16}\text{C}(\text{O})-$, $-(\text{CH}_2)_1\text{OC}(\text{O})\text{NR}^{16}-$, $-(\text{CH}_2)_1\text{NR}^{16}\text{C}(\text{O})\text{NR}^{16}-$ in which the groups R^{16}

15

are the same or different), $-(\text{CH}_2)_1\text{O}-$, $-(\text{CH}_2)_1\text{SO}_3-$ and a bond, in which 1 is from 1 to 12 and R^{16} is selected from the group consisting of hydrogen and C_1 - C_4 alkyl groups; and

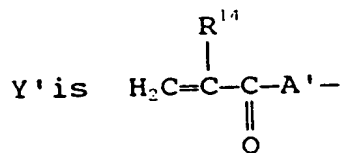
Q is selected from the group consisting of straight and branched alkyl, alkoxyalkyl and (oligo-alkoxy)alkyl groups containing 6 to 24 carbon atoms, any of which groups is unsubstituted or substituted by one or more fluorine atoms and optionally contains one or more carbon-carbon double or triple bonds; and

20

siloxane groups $-(\text{CR}^{16a})_{qq}(\text{SiR}^{16b})_p(\text{OSiR}^{16b})_{pp}\text{R}^{16b}$ in which each group R^{16a} is the same or different and is selected from the group consisting of hydrogen, alkyl groups of 1 to 4 carbon atoms and aralkyl groups, each group R^{16b} is alkyl of 1 to 4 carbon atoms, qq is from 1 to 6 and pp is from 0 to 49.

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30 6. A process according to claim 5 in which



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in which R^{14} is methyl and A' is $-\text{O}-$ and Q is an alkyl group of the formula $-(\text{CR}^{17})_m\text{CR}^{17}$, wherein the groups $-(\text{CR}^{17})_m-$ are the same or different and in each group $-(\text{CR}^{17})_m-$ the groups R^{17} are the same or different and each group R^{17} is selected

from the group consisting of hydrogen, C₁₋₄-alkyl and -fluoroalkyl and fluorine and m is in the range 5 to 23.

7. A process according to claim 6 in which the said comonomer is selected from the group consisting of n-
5 dodecyl methacrylate, octadecyl methacrylate, hexadecyl methacrylate, 1H,1H,2H,2H-heptadecafluorodecyl methacrylate, p-octyl styrene, p-dodecyl styrene and monomethacryloxypropyl terminated siloxanes.

8. A process according to claim 7 in which the said
10 comonomer is dodecyl methacrylate.

9. A process according to claim 1 in which the said radical polymerisable monomers include a diluent monomer selected from the group consisting of C₁₋₄-alkyl(alk)acrylates, N,N-dialkylamino alkyl(alk)acrylates
15 containing 1 to 4 carbon atoms in each N-alkyl group and 1 to 4 carbon atoms in the alkylene group, C₁₋₄-alkyl(alk)acrylamide, hydroxy C₁₋₄-alkyl(alk)acrylate, N-vinyl lactam having 5-7 atoms in the lactam ring, styrene, derivatives of styrene having ring substituents
20 selected from C₁₋₄-alkyl groups and halogen atoms, polyhydroxyl (alk)acrylates, alkenes, butadiene, maleic anhydride and acrylonitrile.

10. A process according to claim 9 in which the diluent monomer is selected from hydroxy C₁₋₄-alkyl(alk)acrylates
25 and polyhydroxyl(alk)acrylates.

11. A process according to claim 1 in which the said radical polymerisable monomers include at least 5% by weight zwitterionic monomer and at least 0.1% by weight monomer having a reactive group.

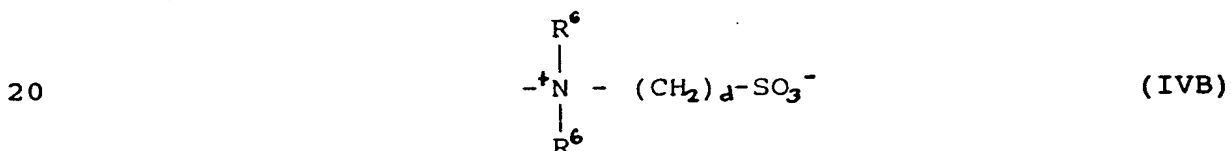
30 12. A process according to claim 9 in which the said radical polymerisable monomers include at least 5% by weight zwitterionic monomer, at least 0.1% by weight monomer having a reactive group and 5 to 20% by weight diluent monomer.

35 13. A process according to claim 5 in which the said radical polymerisable monomers include at least 5% by weight zwitterionic monomer, at least 0.1% by weight

monomer having a reactive group and 5 to 90% by weight of said comonomer.

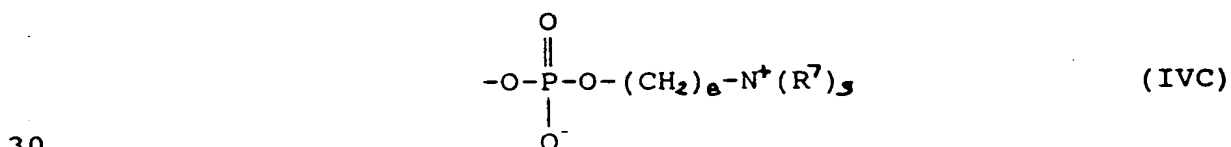
14. A biocompatibilising process in which a substrate having a surface which bears substrate pendant functional groups is biocompatibilised by coating it with a coating composition containing a polymer formed from a radical polymerisable monomers including a radical polymerisable zwitterionic monomer and a radical polymerisable monomer containing a reactive group to form a polymer having zwitterionic groups and pendant reactive groups and the said pendant reactive groups are reacted to form covalent bonds with said substrate pendant functional group and thereby form a stable coating of polymer on the said surface.

15. A process according to claim 14 in which the zwitterionic group is a group X selected from groups IVB, IVC, IVD, IVE and IVF in which group IVB has the formula



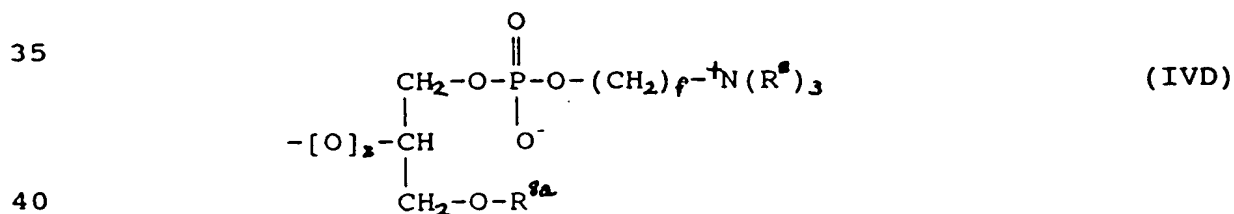
wherein the groups R⁶ are the same or different and each is hydrogen or C₁₋₄ alkyl and d is from 2 to 4;

group IVC has the formula



where the groups R⁷ are the same or different and each is hydrogen or C₁₋₄ alkyl, and e is from 1 to 4;

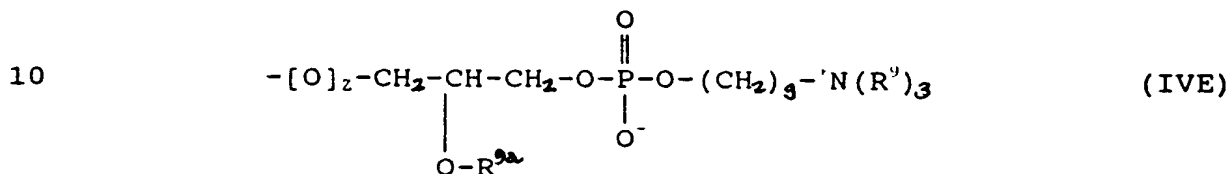
group IVD has the formula



wherein the groups R⁸ are the same or different and each is hydrogen or C₁₋₄ alkyl, R^{8a} is hydrogen or a group -C(O)B¹R^{8b}

wherein R^{2a} is hydrogen or methyl, B^1 is a valence bond or straight or branched alkylene, oxaalkylene or oligo-oxaalkylene group, and f is from 1 to 4; and if B is other than a valence bond z is 1 and if B is a valence bond z is 0, if X is directly bonded to an oxygen or nitrogen atom and otherwise z is 1;

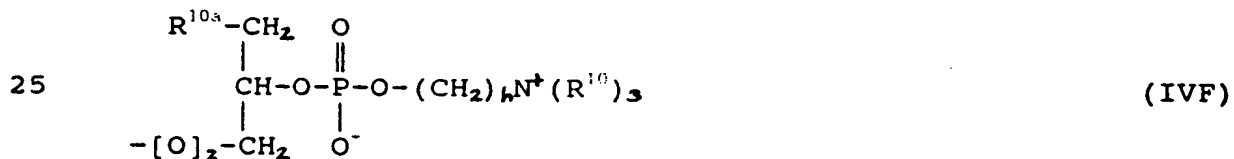
group IVE has the formula



wherein the groups R^9 are the same or different and each is hydrogen or C_1 - C_4 alkyl, R^{2a} is hydrogen or a group $-C(O)B^2R^{2b}$, wherein R^{2b} is hydrogen or methyl, B^2 is a valence bond or a straight or branched alkylene, oxaalkylene or oligo-oxaalkylene group, and g is from 1 to 4; and

if B is other than a valence bond z is 1 and if B is a valence bond z is 0 if X is directly bonded to an oxygen or nitrogen atom and otherwise z is 1; and

group IVF has the formula



wherein the groups R^{10} are the same or different and each is hydrogen or C_1 - C_4 alkyl, R^{10a} is hydrogen or a group $-C(O)B^3R^{10b}$ wherein R^{10b} is hydrogen or methyl, B^3 is a valence bond or a straight or branched alkylene, oxaalkylene or oligo-oxaalkylene group, and h is from 1 to 4; and

if B is other than a valence bond z is 1 and if B is a valence bond z is 0 if X is directly bonded to the oxygen or nitrogen and otherwise z is 1.

16. A process according to claim 14 in which the pendant functional group on the polymer is a group Q^3 selected from the group consisting of aldehyde groups; silane and siloxane groups containing one or more substituents selected from halogen atoms and C_1 - C_4 -alkoxy groups;

hydroxyl; amino; carboxyl; epoxy; $-\text{CHOHCH}_2\text{Hal}$ (in which Hal is selected from chlorine, bromine and iodine atoms); succinimido; tosylate; triflate; imidazole carbonyl amino; optionally substituted triazine groups; aceoxy; mesylate; carbonyl di(cyclo)alkyl carbodiimidoyl; and oximino.

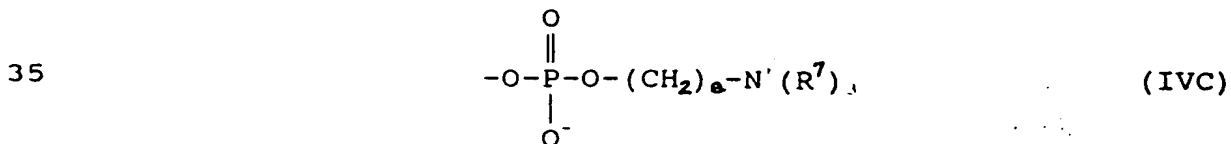
17. A process according to claim 15 in which the pendant functional group on the polymer is a group Q^3 selected from the group consisting of aldehyde groups; silane and siloxane groups containing one or more substituents selected from halogen atoms and C_{1-4} -alkoxy groups; hydroxyl; amino; carboxyl; epoxy; $-\text{CHOHCH}_2\text{Hal}$ (in which Hal is selected from chlorine, bromine and iodine atoms); succinimido; tosylate; triflate; imidazole carbonyl amino; optionally substituted triazine groups; aceoxy; mesylate; carbonyl di(cyclo)alkyl carbodiimidoyl; and oximino.

18. A process according to claim 16 in which the pendant functional group is selected from the group consisting of aldehyde, reactive silane and siloxane amino, epoxy, $\text{CHOHCH}_2\text{Hal}$ (in which Hal is halogen), succinimido, tosylate, triflate, imidazolecarbonyl amino and optionally substituted triazine groups.

19. A process according to claim 17 in which the pendant functional group is selected from the group consisting of aldehyde, reactive silane and siloxane amino, epoxy, $\text{CHOHCH}_2\text{Hal}$ (in which Hal is halogen), succinimido, tosylate, triflate, imidazolecarbonyl amino and optionally substituted triazine groups.

20. A process according to claim 14 in which the surface pendant groups are selected from the group consisting of hydroxyl, carboxyl and amine groups.

21. A process according to claim 14 in which the zwitterionic group is a group of formula IVC



where the groups R^7 are the same or different and each is hydrogen or C_{1-4} alkyl, and e is from 1 to 4;

the pendant functional group of the polymer is an amine group and

the pendant functional group on the substrate surface is a carboxyl group and in which the said covalent bond
5 which is formed is an amide bond.